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(54) **Process for preparing imidized acrylic polymers**

(57) An improved process for preparing imidized (meth)acrylate polymers is carried out continuously by reacting a (meth)acrylate polymer with ammonia or a primary amine in an internally baffled tubular reaction vessel.

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SPECIFICATION

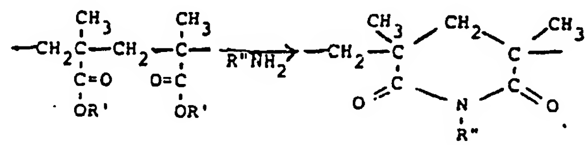
Process for preparing imidized acrylic polymers

Field of the invention

This invention relates to a process for imidizing acrylic polymers; and more particularly to a continuous process carried out in an internally baffled tube.

Background of the invention

Methyl methacrylate (MMA) homopolymer and copolymers with, e.g., acrylates, styrene or butadiene, can be imidized by reacting the polymer with ammonia or alkyl- or aryl- amines to form imides as shown in the equation following:



The cyclic imide polymers can also be obtained by heating selected amides or nitriles. Most such processes are batch operations. Recently a continuous imidization procedure was described in U.S. Patent 4,246,374 in which a methacrylate or acrylate polymer is placed in a vented screw extruder with an amine and the imide is formed as the materials are moved through the extruder at elevated temperatures under essentially anhydrous conditions.

Summary of the invention

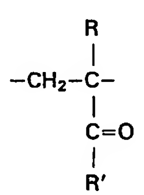
A novel continuous process for imidizing methacrylic and acrylic resins has now been found which does not need to employ a screw extruder and in which temperature and pressure can be more carefully controlled than in a screw extruder.

The novel process is a process for imidizing a methacrylate or acrylate polymer which comprises in sequence

a) mixing a molten methacrylate or acrylate polymer with ammonia or an alkyl- or aryl- primary amine.
b) introducing the molten mixture into a baffled tubular reactor which provides dispersed plug-flow,
c) raising the temperature of the mixture inside the tubular reactor to between 200°C and 300°C, and
d) conducting the molten mixture through the tubular reactor in a time adequate to accomplish imidization but less than necessary for substantial degradation of polymer.

Description of the invention

The polymer to be imidized is an acrylic and/or methacrylic polymer. It contains adjacent units of



wherein R is $-CH_3$ or $-H$, and R′ is alkyl of 1-10 carbon atoms. These polymers may also contain units derived from up to 40% by weight methacrylic or acrylic acid, styrene, butadiene, ethylene or acrylonitrile and the like. Polymers containing at least 75% methyl methacrylate are preferred. The molecular weight of the polymers may vary over a wide range. Those having an inherent viscosity of at least 0.3 measured in a .5% solution of mixture of methanol and methylene chloride (20/80) at 25°C are preferred. The polymer to be imidized may be employed in any form, but generally the polymer is in the form of powder or granules prior to melting.

The ammonia or alkyl- or aryl- primary amine employed generally will have the formula $R''NH_2$ wherein R″ is $-H$, alkyl of 1-12 carbon atoms, cycloalkyl of 7 to 11 carbon atoms or aryl of 6-10 carbon atoms, preferably phenyl. Examples of amines useful herein included methyl, ethyl, n-propyl, n-butyl, heptyl, hexyl, octyl, nonyl, decyl, dodecyl, hexadecyl, octadecyl, isobutyl, sec-butyl, t-butyl, isopropyl, 2-ethylhexyl, phenethyl, allyl, benzyl, para-chlorobenzyl and dimethoxyphenethyl amines; besides, alanine, glycine, 3′-aminoacetophenone, 2-aminoanthraquinone and p-aminobenzoic acid. Other suitable amines are cyclohexylamine, 2-amino-4,6-dimethylpyridine, 3-aminophthalimide, 2-aminopyrimidine, 2-aminothiazole, 5-aminothiazole, 5-amino-1-H-tetrazole, aniline, bromoaniline, dibromoaniline, tribromoaniline, chloroaniline, dichloroaniline, trichloroaniline, p-phenetidine and p-toluidine.

In the process of this invention the polymer in molten form and ammonia or amine are mixed just prior to or just after entry into the tubular reactor. One method of mixing is to feed the polymer into an extruder to

melt the polymer and to propel the molten polymer into the tubular reactor. Once the polymer is melted, the ammonia or amine can be added. Care is taken to add the ammonia or amine just prior to or just after entry into the tubular reactor. Addition earlier than that may lead to some premature reaction, thus rendering useless the careful temperature and pressure control obtained by carrying out the reaction in the tubular reactor.

Temperatures of reaction are as low as can be used to maintain a short reaction time and as high as can be tolerated to avoid excessive degradation of the polymer. Use of an internally baffled tubular reactor with high efficiency of mixing and the attendant uniformity of temperatures across contained materials permit the use of short reaction times at relatively high temperatures without fear of hot spots in the reaction medium. Such hot spots and uneven radial temperature distribution result in degradation of the polymer and otherwise unacceptable or undesirable polymeric material. Where residence time of contained materials can be maintained practically constant and where temperatures gradients perpendicular to the axis of flow can be maintained very low, it has been found advantageous to conduct the reaction at high temperatures with short time rather than at low temperatures with longer time.

Important factors for successfully accomplishing the reaction include close overall control of the temperature of reactant materials and maintenance of a short and uniform residence time of materials in the reactor. If there are large temperature differences within the reactant melt, there will be inconsistent degrees of reaction, i.e., incomplete reaction in low temperature zones and polymer degradation in high temperature zones. In a tubular reactor, the temperature differences perpendicular to gross material flow (radially) must be minimized. To minimize such temperature differences, there must be efficient radial dispersion of materials in order that heat transfer will occur from one location in the reactor, radially, to another. Axial temperature control is also important to prevent inconsistent degrees of reaction which might arise from varying exposure to proper temperatures of reaction. A steady state operation is necessary for conducting acceptable continuous reaction processes. A reactor which exhibits the required temperature control, efficiency in heat transfer, and uniformity of residence time, is a tubular reactor internally fitted with a series of helix baffles of alternating opposite pitch. Such a reactor is disclosed in U.S. Patent No. 3,286,992.

To achieve a polymer of uniform quality, it is important that all of the reactant material be exposed to substantially the same reaction temperatures for substantially the same time. This is defined as "dispersed plug flow". Such dispersed plug flow provides that each element of molten polymer is in the reactor for substantially the same time and that there is considerable movement of domains of the molten polymer with respect to other domains of the molten polymer in a radial direction, rather than in an axial or longitudinal direction.

In the present process, the polymer is heated to the reaction temperature prior to entry into the reactor, and the ammonia or amine is added just prior to or just after entry. In the reactor, the temperature is maintained at 200°C to 300°C, preferably 240° to 280°C. In the reactor the reactants are intimately mixed and each element of material experiences practically the same reaction temperature for practically the same duration. The duration of reaction is generally less than about ten minutes and more than about one-quarter minute. The most preferred duration is from about five minutes to about one-half minute - the shorter maximum time being important to prevent excessive degradation, crosslinking, and other undesirable side reactions.

It has been found that close temperature control, small radial temperature gradients, and uniform, short residence time permit good reaction without excessive degradation which would be expected at the high temperature. On completion of the reaction, the resulting imide is removed and volatiles vented. The resulting imide is then cooled and cut into pellets.

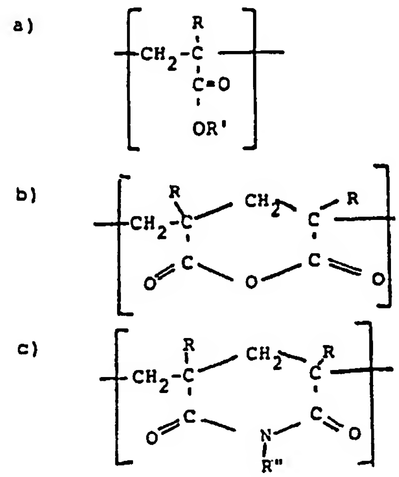
The degree of imidization of the acrylic polymer can easily be controlled in the process according to the invention and various degrees of imidization can be reached as a function of the desired properties. The desired degree of imidization can be adjusted easily through adjustment of the reaction parameters, such as the dwell time and the temperature. Although imidization of the polymer as low as only 1% is possible, as a rule, an imidization of at least 10% is effected, to reach a noteworthy improvement in properties of the acrylic polymer.

No catalyst is required in the process according to the invention. This has the great advantage that removal of the catalyst is dispensed with. However, small quantities of a catalyst can increase the reaction velocity if desired.

A solvent is not necessary in the process of this invention and it is preferred to operate in the absence of a solvent. However, if desired, a solvent may be used to decrease the viscosity of the molten mass or to carry a catalyst.

The imides made by the process of this invention are useful as thermoplastic molding resins, and can be extruded in the form of fibers, tubes or film and the like. The molding resins can be used to prepare molded articles such as toys, pens, housings, etc.

The process of this invention is particularly useful in preparing imides which contain 1-40 weight percent cyclic anhydride units. These imides thus contain recurring units of



wherein R is $-CH_3$ or $-H$; R' is alkyl of 1-10 carbon atoms; and R" is H, alkyl of 1-10 carbons, cycloalkyl of 7-11 carbons, cyclophenyl, or phenylalkyl of 7-9 carbon atoms wherein the phenol groups can contain lower alkyl, lower alkoxy or halo substituents; and wherein units of a) constitute 20 to 94 weight percent of the recurring units, units of b) constitute 1-40 weight percent of the recurring units, and units of c) constitute 5-80 weight percent of the recurring units, said percents totaling 100%.

Description of preferred embodiments

In the following examples, polymer is heated and fed to and through a baffled tubular reactor by means of force provided by a screw extruder. The internally-baffled tubular reactor exhibiting dispersed plug flow used in the examples was supplied by the Kenics Corporation, Danvers, Mass., U.S.A.

A one-inch Killian® extruder with a vacuum port and two-stage screw was fitted at its die exit with with an adaptor plate, three one-inch diameter Kenics Thermogenizer® sections in succession followed by a valve die. The Killian extruder was used to melt and move the polymer into the Kenics section. A diffusion plate 1/8" thick with 64 holes was placed in the leading Kenics edge. This plate, used to aid mixing, was about 1" downstream of an injection probe exiting 1/4" into the melt stream (fitted into an adaptor plate) and about 1 1/2" upstream of the first element of the first Kenics section. Ammonia or amine was entered through the injection probe or through the vent port of the Killian extruder. A screen pack was placed after the last Kenics section and before the valve die to aid in pressure control. A heated transfer pipe was used to convey the melt from the valve die to the rear vacuum part of a Werner and Pfliederer 28-mm twin screw extruder which was used to remove volatiles. The feed throat of the 28-mm extruder was used as a vacuum to vent volatiles and the front vacuum port was used to devolatilize the imide product as well. The emerging imide strand was then quenched and cut.

Unless otherwise indicated, percentages are by weight.

Example 1

This example demonstrates that the imidization reaction occurs in the baffled tubular reactor and not in either of the extruders. Two fine (DY) and two coarse (CY) Koch® baffled plug-flow mixers replaced the leading Kenics elements in the first of the three Kenics sections and two coarse (CY) Koch® elements replaced the leading Kenics elements in the second Kenics section. The 1" Killian extruder was run at 144 rpm with temperature settings of 250°C rear zone, 225°C center zone, and 225°C front zone. The Kenics section were all set to provide a temperature of 280°C; the die valve and the transfer pipe were set at 225°C. The 28-mm twin screw extruder had a straight through screw design with the exception of one set of reverse elements between the two regular vacuum ports to provide a melt seal. It was run between 108 and 135 rpm with the following temperature settings: (1) = 50°C, (2) = 200°C, (3), (4), (5), and die = 250°C.

Four batches were run using cyclohexyl amine and polymethyl methacrylate of IV of between .47 and .53. During batches 1 and 2 the amine was pumped into the vacuum port of the 1" Killian extruder; during batches 3 and 4, it was pumped into the injection probe set into the adaptor plate. In batches 1 and 3 the final product was isolated as cut pellets after it was devolatilized in the 28-mm extruder. For batches 2 and 4 samples were removed from a melt thermocouple hole at the downstream end of the transfer pipe just prior to where the melt would come in contact with the screw of the twin screw extruder. Table 1 shows that 63% of the amine reacted with polymer when mixed solely in the tubular reactor (batches 3 and 4) and that only 57% of the amine reacted with polymer when amine was entered into the Killian extruder and product was

passed through the twin extruder (batch 1). Since higher conversion was obtained in batches 3 and 4 than in batch 1, one can conclude that the reaction occurs in the tubular reactor.

TABLE 1

Batch	Pump Pressure (psi)	Amine Pumped In At: (ml/min)	Finished Polymer Production Rate (g/min)	% N in Final Product	% Imide	Amine Conversion
1	900	12.5	38.6	2.24	37.5	57%
2	900	12.5	"*	2.3f5	39.3	Not Measured
3	900	12.0	41.4	2.22	37.3	63%
4	900	12.0	"*	2.22	37.3	63%

* Could not be actually measured but no controls were changed during short term of these states; therefore, rates probably unchanged.

Example 2

The same apparatus was used as in Example 1 except only two DY Koch® mixers in the leading portion of the first Kenics section replaced any Kenics elements. The one-inch Killian extruder was run at 145 rpm with temperature settings of 175°C (rear), 225°C (center), and 250°C (front). The temperature of the three Kenics sections was set at 280°C. The 28-mm twin screw extruder was run at 130 rpm with the following temperatures being recorded: 1 - 140°C (rear), 2 - 245°C, 3 - 245°C, 4 - 250°C, 5 - 242°C, and die - 215°C. Cyclohexyl amine was pumped into the vacuum port of the Killian extruder at a rate of 16.1 ml/min at a pressure of 800 psi. A polymer composed of units of methyl methacrylate/styrene/butadiene (70/25/5) was fed to the one-inch extruder and a devolatilized final product produced at a rate of 41.9 g/min which contained 2.58% N nitrogen corresponding to 43.2% N-cyclohexyl imide structure having a Tg of 144°C as determined by DSC.

Example 3

The same apparatus was used as in Example 1 except for the presence of 2DY and 4CY Koch elements in the first Kenics section, 8CY elements in the second, and 2CY elements in the third. The one-inch Killian extruder was run at 144 rpm with temperatures of 250°C (rear), 234°C (center), and 227°C (front). The three Kenics sections were each set at 280°C. The 28-mm twin screw extruder was run at 104 rpm with temperatures of 1 - 153°C (rear), 2 - 247°C, 3 - 275°C, 4 - 277°C, 5 - 273°C, and die - 284°C. Aniline was pumped into the vacuum port of the Killian extruder at 9.5 ml. min. The polymer employed was a copolymer of methyl methacrylate/methacrylic acid (87/13, I.V. in CH_2Cl_2 = 0.53). Imide product was produced at 35 g/min which contained 1.50% nitrogen corresponding to 24.6% N-cyclohexyl imide of methacrylic acid.

Example 4

The same apparatus and temperatures were used as in Example 3. Ammonia was pumped in at the adaptor plate at a rate of 5 g/min. The pressure was controlled by the die valve to a level of 2000 psi. Polymer was introduced at a rate of 40 g/min. The polymer employed was a terpolymer having the components methyl methacrylate/styrene/butadiene in a weight ratio of approximately 75/20/5, with an I.V. in CH_2Cl_2 of 0.51. The imidized resin produced contained 4.65% N and had a Tg of 159°C.

Example 5

This example demonstrates reaction of cyclohexylamine and methacrylate polymer to form both cyclic imide and anhydride units.

The one-inch Killian extruder was run at 144 rpm with temperature settings of 250°C rear, 225°C center and front zone. The baffled tubular reactor employed comprised the three Kenics sections. In section 1, the Kenics baffles were replaced with Koch DY and CY baffles. In section 2, the first Kenics baffle was replaced with a Koch CY baffle. The sections were set at 280°C. The valve die and transfer pipe were set at 225°C. The 28 mm W-P extruder had a straight through screw design with the exception of one set of reverse elements between the regular vacuum ports to provide a melt seal and was run at 108-135 rpm with temperature settings of 50°C (rear), 200°C (center) and 250°C (die).

A copolymer of methyl methacrylate and ethyl acrylate (95.5/4.5%) with an inherent viscosity of 0.575 was fed to the 1" extruder at about 37 g/min and cyclohexyl amine pumped in at point A (the vacuum port of the Killian extruder) or point B (the injection probe), at 900 psi and at about 10.4 g/min (22 wt %). Imidized polymer was removed for sampling as it existed the baffled tubular reactor (Point I) or devolatilization in the twin screw extruder (Point II). Results were as follows:

	Amine Addition Point	Polymer Sample Point	Imide Units*	Anhydride** Units
1	A	II	37.5 wt %	7.5 wt %
2	A	I	39.3	5.2
3	B	II	37.3	5.6
4	B	I	37.3	5.6

*Imide content from nitrogen analysis and infrared spectra
**Anhydride content from titration and infrared spectra.

CLAIMS

1. A process of imidizing a methacrylate or acrylate polymer which comprises, in sequence
a) mixing a molten methacrylate or acrylate polymer with ammonia or an aliphatic or aromatic primary amine,
b) introducing the molten mixture into a baffled tubular reactor which provides dispersed plug-flow,
c) raising the temperature of the mixture inside the tubular reactor to between 200° and 300°C, and
d) conducting the molten mixture through the tubular reactor in a time adequate to accomplish imidization but less than necessary for substantial degradation of polymer.
2. A process according to claim 1 wherein in step c), the temperature is 240 to 280°C.
3. A process according to claim 1 or 2 wherein the polymer is composed of at least 80% by weight methyl methacrylate units.
4. A process according to claim 1, 2 or 3 wherein the polymer is mixed in step a) with cyclohexylamine or ammonia.
5. A process according to claim 1 substantially as described in any one of the Examples.

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